

# PHILOSOPHICAL TRANSACTIONS.

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I. *The Bakerian Lecture, on some chemical Agencies of Electricity.*  
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## 1. *Introduction.*

THE chemical effects produced by electricity have been for some time objects of philosophical attention; but the novelty of the phenomena, their want of analogy to known facts, and the apparent discordance of some of the results, have involved the enquiry in much obscurity.

An attempt to elucidate the subject will not, I hope, be considered by the Society as unfitted to the design of the Bakerian Lecture. I shall have to detail some minute (and I fear tedious) experiments; but they were absolutely essential to the investigation. I shall likewise, however, be able to offer some illustrations of appearances which hitherto have not been fully explained, and to point out some new properties of one of the most powerful and general of material agents.

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## II. *On the Changes produced by Electricity in Water.*

The appearance of acid and alkaline matter in water acted on by a current of electricity, at the opposite electrified metallic surfaces was observed in the first chemical experiments made with the column of VOLTA.\*

Mr. CRUICKSHANK† supposed that the acid was the nitrous acid and the alkali ammonia. M. DESORMES‡ soon after attempted to show by experiments, that muriatic acid and ammonia were the products, and M. BRUGNATELLI§ asserted the formation of a new and peculiar substance, which he has thought proper to call the electric acid. The experiments said to be made in Italy, and in this country, on the production of muriate of soda are recent,|| and the discussions with regard to them still alive. As early as 1800, I had found that when separate portions of distilled water, filling two glass tubes connected by moist bladders, or any moist animal or vegetable substances, were submitted to the electrical action of the pile of VOLTA by means of gold wires, a nitro-muriatic solution of gold appeared in the tube containing the positive wire, or the wire transmitting the electricity, and a solution of soda in the opposite tube ; ¶ but I soon ascertained that the muriatic acid owed its appearance to the animal or vegetable matters employed ; for when the same fibres of cotton were made use of in successive experiments, and washed after every process in a weak solution of nitric acid, the water in the apparatus

\* NICHOLSON's Journal, 4to. Vol. IV. p. 183. † Ibid. Vol. IV. p. 261.

‡ Annales de Chimie, Tom. XXXVII. p. 233. § Phil. Mag. Vol. IX. p. 181.

¶ By M. PACCHIONI, and by Mr. PEEBLE. Phil. Mag. Vol. XXI. p. 279.

|| I shewed the results of the experiment to Dr. BEDDOES at this time ; and mentioned the circumstance to Sir JAMES HALL, Mr. CLAYFIELD, and other friends in 1801.

containing them, though acted on for a great length of time with a very strong power, at last produced no effect upon solution of nitrate of silver.

In cases when I had procured much soda, the glass at its point of contact with the wire seemed considerably corroded ; and I was confirmed in my idea of referring the production of the alkali principally to this source, by finding that no fixed saline matter could be obtained, by electrifying distilled water in a single agate cup from two points of platina connected with the VOLTAIC battery. Similar conclusions with regard to the appearance of the muriatic acid had been formed by the GALVANIC Society of Paris, by Dr. WOLLASTON, who hit upon the happy expedient of connecting the tubes together by well washed asbestos ; and by M. M. BIOT and THENARD.\*

Mr. SYLVESTER, however, in a Paper published in Mr. NICHOLSON's Journal for last August, states, that though no fixed alkali or muriatic acid appears when a single vessel is employed ; yet that they are both formed when two vessels are used. And to do away all objections with regard to vegetable substances or glass, he conducted his process in a vessel made of baked tobacco-pipe clay inserted in a crucible of platina. I have no doubt of the correctness of his results : but the conclusion appears objectionable. He conceives that he obtained fixed alkali, because the fluid after being heated and evaporated left a matter that tinged turmeric brown, which would have happened had it been lime, a substance that exists in considerable quantities in all pipe-clay ; and even allowing the presence of fixed alkali, the materials employed for the manufacture of tobacco-pipes are not at all such as to exclude the combinations of this substance.

\* No. XL. *Du Moniteur*, 1806.

I resumed the enquiry; I procured small cylindrical cups of agate, of the capacity of about  $\frac{1}{4}$  of a cubic inch each. They were boiled for some hours in distilled water, and a piece of very white and transparent amianthus that had been treated in the same way was made to connect them together; they were filled with distilled water, and exposed by means of two platina wires to a current of electricity, from 150 pairs of plates of copper and zinc 4 inches square, made active by means of solution of alum. After 48 hours the process was examined: paper tinged with litmus plunged into the tube containing the transmitting or positive wire was immediately strongly reddened. Paper coloured by turmeric introduced into the other tube had its colour much deepened; the acid matter gave a very slight degree of turbidness to solution of nitrate of silver. The fluid that affected turmeric retained this property after being strongly boiled; and it appeared more vivid as the quantity became reduced by evaporation; carbonate of ammonia was mixed with it, and the whole dried and exposed to a strong heat: a minute quantity of white matter remained, which, as far as my examination could go, had the properties of carbonate of soda. I compared it with similar minute portions of the pure carbonates of potash and soda. It was not so deliquescent as the former of these bodies, and it formed a salt with nitric acid, which like nitrate of soda soon attracted moisture from a damp atmosphere, and became fluid.

This result was unexpected, but it was far from convincing me that the substances which I had obtained were *generated*. In a similar process, with glass tubes, carried on exactly under the same circumstances, and for the same time, I obtained a quantity of alkali which must have been more than twenty

times greater, but no traces of muriatic acid. There was much probability that the agate might contain some minute portion of saline matter, not easily detected by chemical analysis, either in combination, or intimate adhesion in its pores. To determine this, I repeated the experiment a second, a third, and a fourth time. In the second experiment turbidness was still produced by solution of nitrate of silver in the tube containing the acid, but it was less distinct; in the third process it was barely perceptible: and in the fourth the two fluids remained perfectly clear after the mixture. The quantity of alkaline matter diminished in every operation; and in the last process, though the battery had been kept in great activity for three days, the fluid possessed in a very slight degree only the power of acting on paper tinged with turmeric; but its alkaline property was very sensible to litmus paper slightly reddened, which is a much more delicate test: and after evaporation and the process by carbonate of ammonia, a barely perceptible quantity of fixed alkali was still left. The acid matter in the other tube was abundant; its taste was sour; it smelt like water over which large quantities of nitrous gas have been long kept; it did not affect solution of muriate of barytes; and a drop of it placed upon a polished plate of silver left after evaporation a black stain, precisely similar to that produced by extremely diluted nitrous acid.

After these results, I could no longer doubt that some saline matter existing in the agate tubes had been the source of the acid matter capable of precipitating nitrate of silver, and of much of the alkali. Four additional repetitions of the process, however, convinced me that there was likewise some other cause for the presence of this last substance; for it

continued to appear to the last, in quantities sufficiently distinguishable, and apparently equal in every case. I had used every precaution; I had included the tubes in glass vessels out of the reach of the circulating air; all the acting materials had been repeatedly washed with distilled water; and no part of them in contact with the fluid had been touched by the fingers.

The only substance which I could now conceive capable of furnishing the fixed alkali was the *water itself*. This water appeared pure by the tests of nitrate of silver and muriate of barytes; but potash and soda, as is well known, rise in small quantities in rapid distillations; and the New River water, which I made use of, contains animal and vegetable impurities, which it was easy to conceive might furnish neutral salts capable of being carried over in vivid ebullition.

To make the experiment in as refined a form as possible, I procured two hollow cones of pure gold containing about 25 grains of water each, they were filled with distilled water, connected together by a moistened piece of amianthus which had been used in the former experiments, and exposed to the action of a VOLTAIC battery of 100 pairs of plates of copper and zinc of 6 inches square, in which the fluid was a solution of alum and diluted sulphuric acid. In ten minutes the water in the negative tube had gained the power of giving a slight blue tint to litmus paper: and the water in the positive tube rendered it red. The process was continued for 14 hours; the acid increased in quantity during the whole time, and the water became at last very sour to the taste. The alkaline properties of the fluid in the other tube, on the contrary, remained stationary, and at the end of the time, it did not act upon litmus or turmeric paper more than in the first trial: the effect was less vivid after it had been strongly heated for a

minute ; but evaporation and the usual process proved that *some* fixed alkali was present. The acid, as far as its properties were examined, agreed with pure nitrous acid having an excess of nitrous gas.

I repeated the experiment, and carried on the process for three days ; at the end of which time the water in the tube was decomposed and evaporated to more than one half of its original quantity ; the acid was strong, but the alkali in as minute a portion as in the last experiment. It acted indeed rather more vividly on the tests, on account of the greater diminution of the fluid, but presented the same results after being heated.

It was now impossible to doubt that the water contained some substance in very minute quantities, capable of causing the appearance of fixed alkali, but which was soon exhausted ; and the question that immediately presented itself was, Is this substance saline matter carried over in distillation ? or is it nitrogen gas which exists in minute portions in all water that has been exposed to air, and which, if an element of the fixed alkali, would under the circumstance of the experiment have been soon exhausted, whilst its absorption from the atmosphere would be impeded by the saturation of the water with hydrogen ?

I was much more inclined to the former than to the latter supposition. I evaporated a quart of the distilled water that I had used, very slowly at a heat below  $140^{\circ}$  FAHRENHEIT, in a silver still ; a solid matter remained, equal to  $\frac{7}{10}$  of a grain ; this matter had a saline but metallic taste, and was deliquescent when exposed to air : I could not obtain from it regular crystals ; it did not affect turmeric or litmus, but a part

of it, after being heated red, in a silver crucible, exhibited strong alkaline properties. It was not possible to make a minute analysis of so small a quantity, but it appeared to me to be principally a mixture of nitrate of soda and nitrate of lead ; and the metallic substance, it is most likely, was furnished by the condensing tube of the common still.

The existence of saline matter in the distilled water being thus distinct, it was easy to determine its operation in the experiment. I filled the two gold cones with water in the usual manner ; that negatively electrified, soon attained the maximum of its effect upon turmeric paper. I then introduced into it a very minute portion of the substance obtained by the process of evaporation that has been just described ; in less than two minutes its effects were evident ; and in five minutes the tint of the paper was changed to a bright brown.

I now conceived that by collecting the water obtained in the second process of slow distillation I should be able to carry on the experiment without *any* appearance of fixed alkali, and the trial proved that I was not mistaken.

Some of this water was introduced into the gold tubes, and the amianthus moistened by it.

After two hours the water in the negative tube produced no effect upon turmeric paper ; it did produce an effect upon litmus, which it required great minuteness of observation to perceive ; but it wholly lost the power by being heated strongly for two or three minutes, so there is every reason for supposing that it was owing to a small quantity of ammonia.

I made a similar experiment with a portion of the same water in the tubes of agate that had been so often used, and

I had the pleasure of finding the results precisely the same.

To detail any more operations of this kind will be unnecessary; all the facts prove that the fixed alkali is not *generated*, but *evolved*, either from the solid materials employed, or from saline matter in the water.

I have made many experiments in vessels composed of different substances, with the water procured by very slow distillation: and in almost every instance some fixed alkali appeared.

In tubes of wax the alkaline matter was a mixture of soda and potash; and the acid matter a mixture of sulphuric, muriatic, and nitric acids.

In a tube of resin, the alkaline matter seemed to be principally potash.

A cube of Carrara marble of about an inch, having an aperture in its centre, was placed in a crucible of platina, which was filled as high as the upper surface of the cube with the purified water, the aperture was filled with the same fluid; the crucible was positively electrified by a strong VOLTAIC power, and a negatively electrified wire introduced into the aperture.

The water soon gained the property of affecting the tint of turmeric; and fixed alkali and lime were both obtained from it: and this effect took place in repeated experiments: the fixed alkali, however, diminished in quantity every time; and after eleven processes conducted from two to three hours each, disappeared altogether. The production of lime-water was uniform.

I made a solution of 500 grains of this marble in nitric

acid ; I decomposed the mixture by carbonate of ammonia, and I collected and evaporated the fluid part, and decomposed the nitrate of ammonia by heat. About  $\frac{3}{4}$  of a grain of fixed saline matter remained, which had soda for its base.

It was possible that the Carrara marble might have been recently exposed to sea-water ; I therefore tried, in the same way, a piece of granular marble, which I had myself broken from a rock on one of the highest of the primitive mountains of Donegal. It afforded fixed alkali by the agency of negative electricity.

A piece of argillaceous schist from Cornwall, treated in the same manner, gave the same result ; and serpentine from the Lizard, and grauwacke from North Wales, both afforded soda. It is probable that there are few stones that do not contain some minute portions of saline matter, which in many cases may be mechanically diffused through their substance : and it is not difficult to conceive the possibility of this, when we consider that all our common rocks and strata bear evident marks of having been anciently covered by the sea.

I was now able to determine distinctly, that the soda procured in glass tubes came principally from the glass, as I had always supposed.

I used the two cones of gold with the purified water and the amianthus ; the process was conducted as usual. After a quarter of an hour, the negatively electrified tube did not change the colour of turmeric. I introduced into the top of it a bit of glass ; in a few minutes the fluid at the surface rendered the tint of the paper of a deep bright brown.

I had never made any experiments, in which acid matter

having the properties of nitrous acid was not produced, and the longer the operation the greater was the quantity that appeared.

Volatile alkali likewise seemed to be always formed in very minute portions, during the first few minutes in the purified water in the gold cones, but the limit to its quantity was soon attained.

It was natural to account for both these appearances, from the combination of nascent oxygene and hydrogene respectively; with the nitrogene of the common air dissolved in the water: and Dr. PRIESTLEY's experiments on the absorption of gases by water (on this idea) would furnish an easy explanation of the causes of the constant production of the acid, and the limited production of the alkali: for hydrogene, during its solution in water, seems to expel nitrogene; whilst nitrogene and oxygene are capable of co-existing dissolved in that fluid.\*

To render the investigation more complete, I introduced the two cones of gold with purified water under the receiver of an air pump; the receiver was exhausted till it contained only  $\frac{1}{84}$  of the original quantity of air; and then, by means of a convenient apparatus, the tubes were connected with an active VOLTAIC pile of 50 pairs of plates of 4 inches square. The processs was carried on for 18 hours, when the result was examined. The water in the negative tube produced no effect upon prepared litmus, but that in the positive tube gave it a barely perceptible tinge of red.

An incomparably greater quantity of acid would have been formed in a similar time in the atmosphere, and the small

\* PRIESTLEY's Experiments and Observations, Vol. I. page 59.

portion of nitrogene gas remaining in contact with the water, seemed adequate to the effect.

I repeated the experiment under more conclusive circumstances. I arranged the apparatus as before; I exhausted the receiver, and filled it with hydrogene gas from a convenient airholder; I made a second exhaustion, and again introduced hydrogene that had been carefully prepared. The process was conducted for 24 hours, and at the end of this time neither of the portions of the water altered in the slightest degree the tint of litmus.

It seems evident then that water, chemically pure, is decomposed by electricity into gaseous matter alone, into oxygene and hydrogene.

The cause of its decomposition, and of the other decompositions which have been mentioned, will be hereafter discussed.

### *III. On the Agencies of Electricity in the Decomposition of various Compounds.*

The experiments that have been detailed on the production of alkali from glass, and on the decomposition of various saline compounds contained in animal and vegetable substances, offered some curious objects of enquiry.

It was evident, that in all changes in which acid and alkaline matter had been present, the acid matter collected in the water round the positively electrified metallic surface; and the alkaline matter round the negatively electrified metallic surface; and this principle of action appeared immediately related to one of the first phænomena observed in the VOLTAIC pile, the

decomposition of the muriate of soda attached to the paste-board; and to many facts which have been since observed on the separation of the constituent parts of neutrosaline and metallic solutions, particularly those detailed by M. M. HISINGER and BERZELIUS.\*

The first experiments that I made immediately with respect to this subject were on the decomposition of solid bodies, insoluble, or difficultly soluble in water. From the effects of the electrical agency on glass, I expected that various earthy compounds would undergo change under similar circumstances; and the results of the trials were decided and satisfactory.

Two cups made of compact sulphate of lime, containing about 14 grain-measures of water each, were connected together by fibrous sulphate of lime, which was moistened by pure water: the cups were filled with this fluid; platina wires from the VOLTAIC battery of 100 pairs of plates of six inches were introduced into them, so that the circuit of electricity was through the fibrous sulphate of lime. In five minutes the water in the cup connected with the positive wire became acid; that in the opposite cup strongly tinged turmeric. After an hour the fluids were accurately examined; when it was found that a pure and saturated solution of lime had been produced in the cup containing the negative wire, which was partially covered with a crust of lime; and that the other cup was filled with a moderately strong solution of sulphuric acid.

I procured two cubical pieces of crystallized sulphate of strontites, of about an inch; a hole was drilled in each capable of containing about 8 grains of water: the cubes were

\* *Annales de Chimie*, Tom. LI. p. 167.

plunged in pure water in a platina crucible ; and the level of the fluid preserved a few lines below the surface of the cubes ; two platina wires were introduced into the holes, which were filled with pure water. The disengagement of gas, when the wires were connected with the battery of 100, proved that the sulphate of strontites was sufficiently porous to form a proper conducting chain. The results were much longer in being obtained in this experiment than in the last : some time elapsed before a sensible effect could be perceived ; but the termination was similar. In 30 hours the fluid in the cavity containing the negative wire had gained the property of precipitating solution of sulphate of potash ; and the presence of sulphuric acid in the other cavity was evident from its effect upon solution of muriate of barytes.

I made an experiment upon fluate of lime under like circumstances ; but the crystallized fluate not being equally permeable to moisture, the two cavities were connected by moist asbestos. This decomposition was likewise very slow ; but in the course of two days a pretty strong solution of lime was obtained in one tube ; and an acid fluid in the other, which precipitated acetite of lead, and left a spot upon the glass from which it had been evaporated.

Sulphate of barytes, as might be supposed, proved much more difficult of decomposition than either sulphate of strontites or fluate of lime. I had made four or five experiments upon it, with the same kind of apparatus that had been applied to the fluate of lime, before I was able to gain decided results. In the last process performed on this substance, two pieces of a large single crystal were hollowed by grinding, so as to contain about five grains of water each ;

they were connected by moist asbestos, and constantly subjected during four days to the strong action of a battery of 150 pairs of plates of 4 inches square. As the water diminished, its place was supplied by new quantities. At the conclusion of the experiment the fluid on the positive side of the apparatus instantly reddened litmus, tasted very sour, and gave a distinct precipitate with a solution of muriate of barytes; the water on the other side deepened the tincture of turmeric; but did not render solution of sulphate of potash turbid. There was a small quantity of white crust, however, on the sides and the bottom of the cavity, and I conceived that this might be the barytes, which, during the extremely slow decomposition, would have combined with the carbonic acid of the atmosphere. To ascertain if this had been the case, I introduced into the cavity a drop of diluted muriatic acid; a slight effervescence appeared, and the fluid obtained occasioned a distinct white cloudiness in solution of sulphate of soda.

In all these cases the constituent parts of the bodies newly arranged by the effects of electricity existed in considerable quantities, and exposed on a large surface to its action. I had great reason to believe, however, from the trials with distilled water in different vessels, that very minute portions of acid and alkaline matter might be disengaged by this agency from solid combinations, principally consisting of the pure earths.

This part of the investigation was easily elucidated.

For a purpose of geological enquiry, which on a future occasion I shall have the honour of laying before the Society, I had made a careful analysis of a specimen of fine grained basalt from Port Rush in the county of Antrim, by means of

fusion with boracic acid: it had afforded in 100 parts  $3\frac{1}{2}$  parts of soda, and nearly  $\frac{1}{2}$  a part of muriatic acid, with 15 parts of lime. This stone appeared to me very well fitted for the purpose of experiment: cavities were drilled in two pieces, properly shaped; they contained about 12 grains of water each; they were connected by moistened amianthus, and the process conducted as usual with a power of 50 pairs of plates. At the end of ten hours the result was examined with care. The fluid that had been positively electrified had the strong smell of oxymuriatic acid, and copiously precipitated nitrate of silver; the other portion of fluid affected turmeric, and left by evaporation a substance which seemed to be a mixture of lime and soda.

A part of a specimen of compact zeolite, from the Giant's Causeway, which by analysis had given 7 parts in 100 of soda, had a small cavity made in it; it was immersed in pure water in a crucible of platina, and electrified in the same manner as the cube of Carrara marble, mentioned in page 9. In less than two minutes the water in the cavity had gained the property of changing the colour of turmeric; and in half an hour the solution was disagreeably alkaline to the taste. The matter dissolved proved to be soda and lime.

Lepidolite, treated in the same way, gave potash.

A piece of vitreous lava, from Etna, gave alkaline matter, which seemed to be a mixture of soda, potash, and lime.

As in these trials the object was merely to ascertain the general fact of decomposition, the process was never conducted for a sufficient time to develope a quantity of alkaline matter capable of being conveniently weighed, and of course any loss of weight of the substance could not be determined.

I thought it right, however, to make one experiment of this kind, for the sake of removing every possibility of doubt on the source of the different products; and I selected for this purpose glass, as a substance apparently insoluble in water, and not likely to afford in any way erroneous results.

The balance that I employed was made for the Royal Institution, by Mr. FIDLER, after the model of that belonging to the Royal Society; it turns readily with  $\frac{1}{500}$  of a grain when loaded with 100 grains on each side; a glass tube with a platina wire attached, weighing  $84$  grains  $\frac{56}{128}$  was connected with an agate cup, by amianthus; they were filled with purified water, and electrified by a power from 150 pairs of plates, in such a way that the platina in the glass tube was negative. The process was continued for 4 days, when the water was found alkaline. It gave by evaporation and exposure to a heat of about  $400^{\circ}$  FAHRENHEIT, soda mixed with a white powder insoluble in acids, the whole weight of which was  $\frac{36}{128}$  of a grain. The glass tube carefully cleaned and dried weighed  $84$  grains,  $\frac{37}{128}$ . The difference between the loss of weight of the tube and the weight of the products in the water may be easily explained: some minute detached particles of amianthus were present, and the soda must have contained water, a substance which it is probably perfectly free from in glass.

Having obtained such results with regard to the disengagement of the saline parts of bodies insoluble in water, I made a number of experiments on soluble compounds; their decomposition was always much more rapid, and the phænomena perfectly distinct.

In these processes I employed the agate cups with platina wires, connected by amianthus moistened in pure water; the

solutions were introduced into the cups, and the electrifying power applied from batteries of 50 pairs of plates, in the usual way.

A diluted solution of sulphate of potash treated in this manner, produced in four hours at the negative wire a weak lixivium of potash; and a solution of sulphuric acid at the positive wire.

The phænomena were similar when sulphate of soda, nitrate of potash, nitrate of barytes, sulphate of ammonia, phosphate of soda, succinate oxalate, and benzoate of ammonia, and alum were used. The acids in a certain time collected in the tube containing the positive wire, and the alkalies and earths in that containing the negative wire.

Solutions of the muriatic salts, decomposed in the same way, uniformly gave oxymuriatic acid on the positive side.

When compatible mixtures of neutrosaline solutions containing the common mineral acids were used, the different acids and the different bases seemed to separate together in a mixed state, without any respect to the orders of affinity.

When metallic solutions were employed, metallic crystals or depositions were formed, as in common **GALVANIC** experiments, on the negative wire, and oxide was likewise deposited round it; and a great excess of acid was soon found in the opposite cup. With solutions of iron, zinc, and tin, this effect took place, as well as with the more oxidable metals: when muriate of iron was used, the black substance deposited upon the wire was magnetic, and dissolved with effervescence in muriatic acid; and when sulphate of zinc was used, a gray powder possessed of the metallic lustre, and likewise soluble with effervescence, appeared; and in all cases acid in excess was exhibited on the positive side.

Strong or saturated saline solutions, as might have been expected, afforded indications of the progress of decomposition much more rapidly than weak ones; but the smallest proportion of neutrosaline matter seemed to be acted on with energy.

A very simple experiment demonstrates this last principle. If a piece of paper tinged with turmeric, is plunged into pure water in a proper circuit, in contact with the negative point, the very minute quantity of saline compound contained in the paper, affords alkaline matter sufficient to give it instantly a brown tint near its point of contact: and acid in the same manner is immediately developed from litmus paper, at the positive surface.

I made several experiments, with the view of ascertaining whether, in the decompositions by electricity, the separation of the constituent parts was complete from the last portions of the compound; and whenever the results were distinct, this evidently appeared to be the case.

I shall describe one of the most conclusive of the experiments: a very weak solution of sulphate of potash, containing 20 parts water and one part saturated solution, at 64°, was electrified in the two agate cups by the power of 50 pairs of plates for three days: the connecting amianthus, which had been moistened with pure water, was removed, washed with pure water, and again applied, twice every day; by this precaution the presence of any neutral salt that might adhere to it, and disturb the results, was prevented. The alkali obtained in this process in the solution had the properties of pure potash; and when it had been saturated with nitric acid it gave no turbidness by mixture with solution of muriate of

barytes: the acid matter exposed to a strong heat evaporated without leaving any residuum.

*IV. On the Transfer of certain of the constituent Parts of Bodies by the Action of Electricity.*

M. GAUTHEROT has stated,\* that in a single GALVANIC circle of zinc, silver, and water, in an active state, the oxide of zinc formed is attracted by the silver;† and M. M. HISINGER and BERZELIUS detail an account of an experiment, in which solution of muriate of lime being placed in the positive part of a siphon, electrified by wires from a VOLTAIC pile, and distilled water in the negative part, lime appeared in the distilled water.

These facts rendered it probable, that the saline elements evolved in decompositions by electricity were capable of being transferred from one electrified surface to another, according to their usual order of arrangement; but to demonstrate this clearly, new researches were wanting.

I connected one of the cups of sulphate of lime, mentioned page 13, with a cup of agate by asbestos; and, filling them with purified water, made the platina wire in the cup of sulphate of lime transmit the electricity from a power of 100; a wire in the agate cup received it. In about four hours a strong solution of lime was found in the agate cup, and sulphuric acid in the cup of sulphate of lime. By reversing the order, and carrying on the process for a similar time, the sulphuric acid appeared in the agate cup, and the solution of lime on the opposite side.

Many trials were made with other saline substances, with

\* *Annales de Chimie*, Vol. XXXIX. page 203.

† *Ibid.* Vol. LI. page 171.

analogous results. When the compounds of the strong mineral acids with alkaline or alkaline-earthy bases, were introduced into one tube of glass, distilled water connected by amianthus being in another tube, both connected by wires of platina in the VOLTAIC arrangement, the base always passed into the distilled water when it was negative, and the acid when it was positive.

The metals and the metallic oxides passed towards the negative surface like the alkalies, and collected round it. In a case in which solution of nitrate of silver was used on the positive side, and distilled water on the negative, silver appeared on the whole of the transmitting amianthus, so as to cover it with a thin metallic film.

The time required for these transmissions (the quantity and intensity of the electricity, and other circumstances remaining the same) seemed to be in some proportion as the length of the intermediate volume of water. Thus when with the power of 100, sulphate of potash was on the negative side, and distilled water on the positive side, the distance between the wires being only an inch, sulphuric acid, in sufficient quantity to be very manifest, was found in the water in less than five minutes: but when the tubes were connected by an intermediate vessel of pure water, so as to make the circuit 8 inches, 14 hours were required to produce the same effect.

To ascertain whether the contact of the saline solution with a metallic surface was necessary for the decomposition and transfer, I introduced purified water into two glass tubes; a vessel containing solution of muriate of potash was connected with them respectively by amianthus; and the arrangement was made in such a way, that the level of both the portions

of purified water was higher than the level of the saline solution.

In this case, the saline matter was distant from each of the wires at least  $\frac{2}{3}$  of an inch; yet alkaline matter soon appeared in one tube, and acid matter in the other: and in 16 hours moderately strong solutions of potash, and of muriatic acid had been formed.

In this case of electrical transfer or attraction, the acid and alkaline matter seemed to be perfectly pure; and I am inclined to believe that this is uniformly the case in all experiments carefully made. One of the instances in which I conceived acid most likely to be present, was in the transfer of magnesia from sulphate of magnesia in the positive tube, to distilled water in the negative tube. I examined the case, taking care that the distilled water was never upon a lower level than the saline solution: the process was continued for some hours, till a considerable quantity of magnesia had appeared. The connecting amianthus was removed, and muriatic acid poured into the tube: the saturated solution did not precipitate solution of muriate of barytes.

I endeavoured to ascertain the progress of the transfer, and the course of the acid or alkaline matter in these decompositions, by using solutions of litmus and turmeric, and papers coloured by these substances; and these trials led to the knowledge of some singular and unexpected circumstances.

Two tubes, one containing distilled water, the other solution of sulphate of potash, were each connected by amianthus with a small oz. measure filled with distilled water tinged by litmus: the saline solution was negatively electrified; and as it was natural to suppose, that the sulphuric acid in passing

through the water to the positive side would redden the litmus in its course, some slips of moistened paper tinged with litmus were placed above and below the pieces of amianthus, directly in the circuit. The progress of the experiment was minutely observed; the first effect of reddening took place immediately above the positive surface, where I had least expected it; the red tint slowly diffused itself from the positive side to the middle of the vessel, but no redness appeared above the amianthus, or about it, on the negative side, and though it had been constantly transmitting sulphuric acid, it remained unaffected to the last.

The order of the experiment was changed, and the saline solution placed on the positive side; a solution and papers tinged with turmeric being substituted for those tinged with litmus. The effect was precisely analogous; the turmeric became brown first, near the negative wire, and no change took place in the intermediate vessel near the positive wire.

In another process, the two glass tubes were filled with solution of muriate of soda, and the intermediate vessel with solution of sulphate of silver; paper tinged with turmeric was placed on the positive side, and paper tinged with litmus on the negative side; as soon as the electrical circuit was complete, soda began to appear in the negative tube, and oxy-muriatic acid in the positive tube; and the alternate products were exhibited passing into the solution of sulphate of silver, the muriatic acid occasioning a dense heavy precipitate, and the soda a more diffused and a lighter one; but neither the turmeric transmitting the alkali, nor the litmus transmitting the acid, had their tints in the slightest degree altered.

V. *On the Passage of Acids, Alkalies, and other Substances through various attracting chemical Menstrua, by Means of Electricity.*

As acid and alkaline substances during the time of their electrical transfer passed through water containing vegetable colours without affecting them, or apparently combining with them, it immediately became an object of enquiry, whether they would not likewise pass through chemical menstrua, having stronger attractions for them; and it seemed reasonable to suppose, that the same power which destroyed elective affinity in the vicinity of the metallic points, would likewise destroy it, or suspend its operation, throughout the whole of the circuit.

An arrangement was made, of the same vessels and apparatus employed in the experiment on the solution of muriate of soda and sulphate of silver, page 23. Solution of sulphate of potash was placed in contact with the negatively electrified point, pure water was placed in contact with the positively electrified point, and a weak solution of ammonia was made the middle link of the conducting chain; so that no sulphuric acid could pass to the positive point in the distilled water, without passing through the solution of ammonia.

The power of 150 was used: in less than five minutes it was found, by means of litmus paper, that acid was collecting round the positive point; in half an hour, the result was sufficiently distinct for accurate examination.

The water was sour to the taste, and precipitated solution of nitrate of barytes.

Similar experiments were made with solution of lime; and

weak solutions of potash and soda, and the results were analogous. With strong solutions of potash and soda a much longer time was required for the exhibition of the acid ; but even with the most saturated alkaline lixivium, it always appeared in a certain period.

Muriatic acid, from muriate of soda, and nitric acid from nitrate of potash, were transmitted through concentrated alkaline menstrua, under similar circumstances.

When distilled water was placed in the negative part of the circuit, and a solution of sulphuric, muriatic, or nitric acid, in the middle, and any neutral salt with a base of lime, soda, potash, ammonia, or magnesia, in the positive part, the alkaline matter was transmitted through the acid matter to the negative surface, with similar circumstances to those occurring during the passage of the acid through the alkaline menstrua ; and the less concentrated the solution, the greater seemed to be the facility of transmission.

I tried in this way muriate of lime with sulphuric acid, nitrate of potash with muriatic acid, sulphate of soda with muriatic acid, and muriate of magnesia with sulphuric acid ; I employed the power of 150 ; and in less than 48 hours, I gained in all these cases decided results ; and magnesia came over like the rest.

Strontites and barytes passed, like the other alkaline substances, readily through muriatic and nitric acids ; and, *vice versa*, these acids passed with facility through aqueous solutions of barytes and strontites ; but in experiments in which it was attempted to pass sulphuric acid through the *same menstrua*, or to pass barytes or strontites through this acid, the results were very different.

When solution of sulphate of potash was in the negative part of the circuit, distilled water in the positive part, and saturated solution of barytes in the middle, no sensible quantity of sulphuric acid existed in the distilled water after 30 hours, the power of 150 being used; after four days, sulphuric acid appeared, but the quantity was extremely minute; much sulphate of barytes had formed in the intermediate vessel; the solution of barytes was so weak as barely to tinge litmus; and a thick film of carbonate of barytes had formed on the surface of the fluid. With solution of strontites the result was very analogous, but the sulphuric acid was sensible in three days.

When solution of muriate of barytes was made positive by the power of 150, concentrated sulphuric acid intermediate, and distilled water negative. No barytes appeared in the distilled water, when the experiment had been carried on for four days; but much oxymuriatic acid had formed in the positive vessel; and much sulphate of barytes had been deposited in the sulphuric acid.

Such of the metallic oxides as were made subjects of experiment passed through acid solutions from the positive to the negative side, but the effect was much longer in taking place than in the instances of the transition of alkaline matter. When solution of green sulphate of iron was made positive, solution of muriatic acid intermediate, and water negative, in the usual arrangement, green oxide of iron began to appear in about ten hours upon the negative connecting amianthus, and in three days a considerable portion had been deposited in the tube. Analogous results were obtained with sulphate of copper, nitrate of lead, and nitromuriate of tin.

I made several experiments on the transition of alkaline and acid matter through different neutrosaline solutions, and the results were such as might well have been anticipated.

When solution of muriate of barytes was negative, solution of sulphate of potash intermediate, and pure water positive, the power being from 150, sulphuric acid appeared in about five minutes in the distilled water; and in two hours the muriatic acid was likewise very evident. When solution of sulphate of potash was positive, solution of muriate of barytes intermediate, and distilled water negative, the barytes appeared in the water in a few minutes; the potash from the more remote part of the chain was nearly an hour in accumulating, so as to be sensible.

When the solution of muriate of barytes was positive, the solution of sulphate of potash intermediate, and distilled water negative, the potash soon appeared in the distilled water; a copious precipitation of sulphate of barytes formed in the middle vessel; but after ten hours no barytes had passed into the water.

When solution of sulphate of silver was interposed between solution of muriate of barytes on the negative side, and pure water on the positive side, sulphuric acid alone passed into the distilled water; and there was a copious precipitation in the solution of sulphate of silver. This process was carried on for ten hours.

I tried several of these experiments of transition upon vegetable and animal substances with perfect success.

The saline matter exposed in contact with the metal, and that existing in the vegetable or animal substances, both underwent decomposition and transfer; and the time of the appearance of the different products at the extremities of the circuit was governed by the degree of their vicinity.

Thus, when a fresh leaf-stalk of the polyanthus, about 2 inches long, was made to connect a positively electrified tube containing solution of nitrate of strontites, and a negatively electrified tube containing pure water. The water soon became green, and gave indications of alkaline properties, and free nitric acid was rapidly separated in the positive tube. After ten minutes, the alkaline matter was examined ; it consisted of potash and lime, and as yet no strontites had been carried into it : for the precipitate it gave with sulphuric acid readily dissolved in muriatic acid. In half an hour strontites, however, appeared ; and in four hours it formed a very abundant ingredient of the solution.

A piece of muscular flesh of beef, of about 3 inches in length and half an inch in thickness, was treated in the same way as the medium of communication between muriate of barytes and distilled water. The first products were soda, ammonia, and lime ; and after an hour and a quarter, the barytes was very evident. There was much free oxymuriatic acid in the positively electrified tube, but no particle of muriatic acid had passed into the negative tube, either from the muriatic solution or from the muscular fibre.

## VI. *Some general Observations on these Phænomena, and on the Mode of Decomposition and Transition.*

It will be a general expression of the facts that have been detailed, relating to the changes and transitions by electricity, in common philosophical language, to say, that hydrogene, the alkaline substances, the metals, and certain metallic oxides, are attracted by negatively electrified metallic surfaces, and repelled by positively electrified metallic surfaces ; and con-

trariwise, that oxygene and acid substances are attracted by positively electrified metallic surfaces, and repelled by negatively electrified metallic surfaces; and these attractive and repulsive forces are sufficiently energetic to destroy or suspend the usual operation of elective affinity.

It is very natural to suppose, that the repellent and attractive energies are communicated from one *particle to another particle* of the same kind, so as to establish a conducting chain in the fluid; and that the locomotion takes place in consequence; and that this is really the case seems to be shown by many facts. Thus, in all the instances in which I examined alkaline solutions through which acids had been transmitted, I always found acid in them whenever any acid matter remained at the original source. In time, by the attractive power of the positive surface, the decomposition and transfer undoubtedly become complete; but this does not affect the conclusion.

In the cases of the separation of the constituents of water, and of solutions of neutral salts forming the whole of the chain, there may possibly be a succession of decompositions and recompositions throughout the fluid. And this idea is strengthened by the experiments on the attempt to pass barites through sulphuric acid, and muriatic acid through solution of sulphate of silver, in which, as insoluble compounds are formed and carried out of the sphere of the electrical action, the power of transfer is destroyed. A similar conclusion might likewise be drawn from many other instances. Magnesia and the metallic oxides, as I have already mentioned, will pass along moist amianthus from the positive to the negative surface; but if a vessel of pure water be interposed, they do not reach the negative vessel, but sink to the bottom.

These experiments I have very often made, and the results are perfectly conclusive; and in the case, page 26, in which sulphuric acid seemed to pass in small quantities through very weak solutions of strontites and barytes, I have no doubt but that it was carried through by means of a thin stratum of pure water, where the solution had been decomposed at the surface by carbonic acid; for in an experiment similar to these in which the film of carbonate of barytes was often removed and the fluid agitated, no particle of sulphuric acid appeared in the positive part of the chain.

It is easy to explain, from the general phænomena of decomposition and transfer, the mode in which *oxygene* and *hydrogene* are separately evolved from water. The oxygene of a portion of water is attracted by the positive surface, at the same time that the other constituent part, the hydrogene is repelled by it; and the opposite process takes place at the negative surface; and in the middle or neutral point of the circuit, whether there be a series of decompositions and recompositions, or whether the particles from the extreme points only are active, there must be a new combination of the repelled matter: and the case is analogous to that of two portions of muriate of soda separated by distilled water; muriatic acid is repelled from the negative side, and soda from the positive side, and muriate of soda is composed in the middle vessel.

These facts seem fully to invalidate the conjectures of M. RITTER, and some other philosophers, with regard to the elementary nature of water, and perfectly to confirm the great discovery of Mr. CAVENDISH.

M. RITTER conceived that he had procured oxygene from water without hydrogene, by making sulphuric acid the medium of communication at the negative surface; but in this case,

sulphur is deposited, and the oxygene from the acid, and the hydrogene from the water are respectively repelled ; and a new combination produced.

I have attempted some of the experiments of decomposition and transfer, by means of common electricity, making use of a powerful electrical machine of Mr. NAIRNE's construction, belonging to the Royal Institution, of which the cylinder is 15 inches in diameter, and 2 feet long.

With the same apparatus as that employed for decompositions by the VOLTAIC battery, no perceptible effect was produced by passing a strong current of electricity silently for four hours through solution of sulphate of potash.

But by employing fine platina points of  $\frac{1}{75}$  of an inch in diameter, cemented in glass tubes in the manner contrived by Dr. WOLLASTON,\* and bringing them near each other, in vessels containing from 3 to 4 grains of the solution, and connected by moist asbestos, potash appeared in less than two hours round the negatively electrified point, and sulphuric acid round the positive point.

In a similar experiment sulphuric acid was transferred through moist asbestos into water ; so that there can be no doubt, that the principle of action is the same in common and the VOLTAIC electricity.†

\* Phil. Trans. Vol. XCI. page 427.

† This had been shewn, with regard to the decomposition of water, by Dr. WOLLASTON's important researches. — By carefully avoiding sparks, I have been able to obtain the two constituents in a separate state. In an experiment in which a fine platina point cemented in glass, and connected by a single wire with the positive conductor of this machine, was plunged in distilled water in an insulated state, and the electricity dissipated into the atmosphere by means of moistened filaments of cotton, oxygene gas, mixed with a little nitrogen gas, was produced ; and when the same apparatus was applied to the negative conductor hydrogene gas was evolved, and a minute

VII. *On the general Principles of the chemical Changes produced by Electricity*

The experiments of Mr. BENNET had shown, that many bodies brought into contact and afterwards separated, exhibited *opposite* states of electricity; but it is to the investigations of VOLTA that a clear developement of the fact is owing; he has distinctly shown it in the case of copper and zinc, and other metallic combinations; and has supposed that it also takes place with regard to metals and fluids.

In a series of experiments made in 1801,\* on the construction of electrical combinations by means of alternations of single metallic plates, and different strata of fluids, I observed that when acid and alkaline solutions were employed as elements of these instruments, the alkaline solutions always received the electricity from the metal, and the acid always transmitted it to the metal; thus, in an arrangement of which the elements were tin, water, and solution of potash, the circulation of the electricity was from the water to the tin, and from the tin to the solution of potash; but in an arrangement composed of weak nitric acid, water, and tin; the order was from the acid to the tin, and from the tin to the water.

These principles seem to bear an immediate relation to the general phænomena of decomposition and transference, which have been the subject of the preceding details.

portion of oxygene and nitrogenæ gases: but neither of the foreign products, the nitrogenæ gas in the one case and the nitrogenæ and oxygene gases in the other, formed as much as  $\frac{1}{30}$  part of the volume of the gases; and there is every reason to suppose that they were derived from the extrication of common air, which had been dissolved in the water. This result, which when I first obtained it in 1803, appeared very obscure, is now easily explained; the alternate products must have been evolved at the points of the dissipation of the electricity.

\* See Phil. Trans. Vol. XCI. page 397.

In the simplest case of electrical action, the alkali which receives electricity from the metal would necessarily, on being separated from it, appear positive ; whilst the acid under similar circumstances would be negative ; and these bodies having respectively with regard to the metals, that which may be called a positive and a negative electrical energy, in their repellent and attractive functions seem to be governed by laws the same as the common laws of electrical attraction and repulsion. The body possessing the positive energy being repelled by positively electrified surfaces, and attracted by negatively electrical surfaces ; and the body possessing the negative energy following the contrary order.

I have made a number of experiments with the view of elucidating this idea, and of extending its application ; and in all cases they have tended to confirm the analogy in a remarkable manner.

Well burned charcoal water and nitric acid, the same substance water and solution of soda, made respectively elements of different electrical combinations, became distinctly active when 20 alternations were put together : the positive energy being exhibited on the side of the alkali, and the negative on that of the acid. Arrangements of plates of zinc, pieces of moistened pasteboard, and moistened quicklime, to the number of 40 series, likewise formed a weak electrical pile, the effect of the lime being similar to that of an alkali, but the power was soon lost.

I endeavoured, by means of very delicate instruments, to ascertain the electrical states of single insulated acid and alkaline solutions, after their contact with metals ; and for this purpose I employed at different times the condensing

electrometer of Mr. CUTHERBTON's construction, Mr. CAVALLO's multiplier, and a very sensible electrical balance, on the principle of torsion, adopted by M. COULOMB; but the effects were unsatisfactory, the circumstances of evaporation, and of chemical action, and the adherence of the solutions to the surfaces of the metals employed, in most cases, prevented any distinct result, or rendered the source of the electricity doubtful. I shall not enter into any details of these processes, or attempt to draw conclusions from capricious and uncertain appearances, which, as we shall immediately see, may be fully deduced from clear and distinct ones.

The alkaline and acid substances capable of existing in the dry and solid form, give by contact with the metals exceedingly sensible electricities, which require for their exhibition the gold leaf electrometer only with the small condensing plate.

When oxalic, succinic, benzoic or boracic acid, perfectly dry, either in powder or crystals, were touched upon an extended surface with a plate of copper insulated by a glass handle, the copper was found positive, the acid negative. In favourable weather, and when the electrometer was in perfect condition, one contact of the metal was sufficient to produce a sensible charge; but seldom more than five or six were required. Other metals, zinc, and tin for instance were tried with the same effect. And the metal received the positive charge, apparently to the same extent, whether the acid was insulated upon glass, or connected with the ground.

The solid acid of phosphorus, which had been strongly ignited, and most carefully excluded from the contact of air, rendered the insulated plate of zinc positive by four contacts;

but after exposure to the atmosphere for a few minutes it wholly lost this power.

When metallic plates were made to touch dry lime, strontites, or magnesia, the metal became negative ; the effect was exceedingly distinct, a single contact upon a large surface being sufficient to communicate a considerable charge. For these experiments the earths were carefully prepared ; they were in powder, and had been kept for several days in glass bottles before they were used : it is essential to the success of the process that they be of the temperature of the atmosphere. In some experiments which I made upon them when cooling, after having been ignited ; they appeared strongly electrical, and rendered the conductors brought in contact with them positive.

I made several experiments in a similar manner on the effects of the contact of potash and soda with the metals. Potash in no instance afforded a satisfactory result ; its powerful attraction for water presents an obstacle probably unsurmountable to the success of any trials made in the free atmosphere. Soda, in the only case in which electricity was exhibited, affected the metal in the same way as lime, strontites, and magnesia. Upon this occasion the soda had been prepared with great care, exposed in a platina crucible for nearly an hour in a red heat, and suffered to cool in the crucible inverted over mercury ; when cool it was immediately removed, and the contact made with a plate of zinc : the experiment was performed in the open air ; the weather was peculiarly dry, the thermometer stood at 28° FAHRENHEIT, and the barometer at 30.2 inches ; six contacts gave a charge to the condensing electrometer in the first trial ; in the second ten were required to produce a similar effect ; and after this,

though two minutes only had elapsed, no farther result could be obtained.

In the decomposition of sulphuric acid by VOLTAIC electricity the sulphur separates on the negative side. The experiments of various electricians prove, that by the friction of sulphur and metals, the sulphur becomes positive and the metals negative ; the same thing I find happens from the contact of an unexited cake of sulphur and insulated metallic plates. Mr. WILKE has stated an exception to lead, as rendering sulphur negative by its friction. The results that I have obtained with lead, in trials very carefully made, are the same as those with other metals.\* Sulphur, by being rubbed or struck against newly-polished lead, always became positive. Mr. WILKE perhaps was misled by using tarnished lead : sulphur, I find, rubbed against litharge, or lead the surface of which has been long exposed to air, becomes negative ; and this exception being removed, all the facts on the subject are confirmations of the general principle.†

\* As sulphur is a nonconductor, and easily excited by slight friction, or small changes in its temperature, some caution is required in drawing conclusions from the experiments in which it is employed. Sulphur, examined immediately after having been heated, gives a positive charge to conductors, agreeing in this respect with the alkaline substances ; and a slight contact with the dry hand is sufficient to render it negative. In general likewise in experiments of contact care should be taken that the metallic plate is free from electricity : well polished plates of copper and zinc will, I find, receive a negative charge from being laid on a table of common mahogany.

† Concentrated solution of phosphoric acid, I find, is decomposed by VOLTAIC electricity : the phosphorus combines with the negatively electrified metal, and forms a phosphuret ; at least this happened in the two cases that I tried with platina and copper. From all analogy it may be inferred, that the electrical energy of this inflammable substance with regard to metals is the same as that of sulphur. I tried some experiments of contact upon it, but without success. Its slow combustion in the atmosphere it is most likely was the cause of the failure : but even in gases not containing free or loosely combined oxygene, its evaporation would probably interfere.

On the general principle, oxygene and hydrogene ought to possess, with regard to the metals respectively, the negative and positive energy. This I have not been able to prove by direct experiments of contact; but the idea is confirmed by the agency of their compounds; thus I have found that solution of sulphuretted hydrogene in water acts in the electrical apparatus composed of single plates and different strata of fluids, in the same manner as alkaline solutions; and that solution of oxymuriatic acid is more powerful in similar arrangements than solutions of muriatic acid of a higher degree of concentration; and in both these cases, it is impossible to conceive the combined hydrogene and oxygene inactive. The inference likewise is fully warranted by the case of the solutions of alkaline hydroguretted sulphurets, which consisting principally of alkali and sulphur together in union with water, exhibit the positive energy with regard to the metals in a very high degree. In the series of experiments on VOLTAIC arrangements constructed with single plates above-mentioned, I found the solutions of hydroguretted sulphurets in general much more active than alkaline solutions, and particularly active with copper, silver, and lead. And in an experiment that I made on a combination of copper, iron, and hydroguretted sulphurets of potash, in 1802, I found that the positive energy of the hydroguretted sulphurets with regard to the copper was sufficient to overpower that of the iron; so that the electricity did not circulate from the copper to the iron, and from the iron to the fluid, as in common cases, but from the copper to the hydroguretted sulphuret, and from the hydroguretted sulphuret to the iron.

All these details afford the strongest confirmation of the

principle. It may be considered almost as a mere arrangement of facts ; and with some extensions it seems capable of being generally applied.

Bodies possessing opposite electrical energies with regard to one and the same body, we might fairly conclude would likewise possess them with regard to each other. This I have found by experiment is the case with lime and oxalic acid. A dry piece of lime, made from a very pure compact secondary limestone, and of such a form as to present a large smooth surface, became positively electrical by repeated contacts with crystals of oxalic acid : and these crystals placed upon the top of a condensing electrometer, and repeatedly touched by the lime, which after each contact was freed from its charge, rendered the gold leaves negatively electrical. The tendency of the mere contacts of the acid and alkali with the metal would be to produce opposite effects to those exhibited, so that their mutual agency must have been very energetic.

It will not certainly be a remote analogy to consider the other acid and alkaline substances generally, and oxygene and hydrogene as possessing similar electrical relations ; and in the decompositions and changes presented by the effects of electricity, the different bodies naturally possessed of chemical affinities appear incapable of combining, or of remaining in combination, when placed in a state of electricity different from their natural order. Thus, as we have seen, the acids in the positive part of the circuit, separate themselves from alkalies, oxygene from hydrogene, and so on ; and metals on the negative side, do not unite to oxygene, and acids do not remain in union with their oxides ; and in this way the attrac-

tive and repellent agencies seem to be communicated from the metallic surfaces throughout the whole of the menstruum.

### VIII. *On the Relations between the electrical Energies of Bodies, and their chemical Affinities.*

As the chemical attraction between two bodies seems to be destroyed by giving one of them an electrical state different from that which it naturally possesses ; that is, by bringing it artificially into a state similar to the other, so it may be increased by exalting its natural energy. Thus, whilst zinc, one of the most oxidable of the metals, is incapable of combining with oxygene when negatively electrified in the circuit, even by a feeble power ; silver, one of the least oxidable, easily unites to it when positively electrified ; and the same thing might be said of other metals.

Amongst the substances that combine chemically, all those, the electrical energies of which are well known, exhibit opposite states ; thus, copper and zinc, gold and quicksilver, sulphur and the metals, the acid and alkaline substances, afford apposite instances ; and supposing perfect freedom of motion in their particles or elementary matter, they ought, according to the principles laid down, to attract each other in consequence of their electrical powers. In the present state of our knowledge, it would be useless to attempt to speculate on the remote cause of the electrical energy, or the reason why different bodies, after being brought into contact, should be found differently electrified ; its relation to chemical affinity is, however, sufficiently evident. May it not be identical with it, and an essential property of matter ?

The coated glass plates of BECCARIA strongly adhere to each other when oppositely charged, and retain their charges on being separated. This fact affords a distinct analogy to the subject; different particles in combining must still be supposed to preserve their peculiar states of energy.

In the present early stage of the investigation, it would be improper to place unbounded confidence in this hypothesis; but it seems naturally to arise from the facts, and to coincide with the laws of affinity, so ably developed by modern chemists; and the general application of it may be easily made.

Supposing two bodies, the particles of which are in different electrical states, and those states sufficiently exalted to give them an attractive force superior to the power of aggregation, a combination would take place which would be more or less intense according as the energies were more or less perfectly balanced; and the change of properties would be correspondently proportional.

This would be the simplest case of chemical union. But different substances have different degrees of the same electrical energy in relation to the same body: thus the different acids and alkalies are possessed of different energies with regard to the same metal; sulphuric acid, for instance, is more powerful with lead than muriatic acid, and solution of potash is more active with tin than solution of soda. Such bodies likewise may be in the same state or repellent with regard to each other, as apparently happens in the cases just mentioned; or they may be neutral; or they may be in opposite or attracting states, which last seems to be the condition of sulphur and alkalies that have the same kind of energy with regard to metals.

When two bodies repellent of each other act upon the same body with different degrees of the same electrical attracting energy, the combination would be determined by the degree; and the substance possessing the weakest energy would be repelled; and this principle would afford an expression of the causes of elective affinity, and the decompositions produced in consequence.

Or where the bodies having different degrees of the same energy, with regard to the third body, had likewise different energies with regard to each other, there might be such a balance of attractive and repellent powers as to produce a triple compound; and by the extension of this reasoning, complicated chemical union may be easily explained.

Numerical illustrations of these notions might be made without difficulty, and they might be applied to all cases of chemical action; but in the present state of the enquiry, a great extension of this hypothetical part of the subject would be premature.

The general idea will, however, afford an easy explanation of the influence of affinity by the masses of the acting substances, as elucidated by the experiments of M. BERTHOLLET; for the combined effect of many particles possessing a feeble electrical energy, may be conceived equal or even superior to the effect of a few particles possessing a strong electrical energy: and the facts mentioned, page 25, confirm the supposition: for concentrated alkaline lixivia resist the transmission of acids by electricity much more powerfully than weak ones.

Allowing combination to depend upon the balance of the natural electrical energies of bodies, it is easy to conceive that

a *measure* may be found of the artificial energies, as to intensity and quantity produced in the common electrical machine, or the VOLTAIC apparatus, capable of destroying this equilibrium; and such a measure would enable us to make a scale of electrical powers corresponding to degrees of affinity.

In the circuit of the VOLTAIC apparatus, completed by metallic wires and water, the strength of the opposite electricities diminish from the points of contact of the wires towards the middle point in the water, which is necessarily neutral. In a body of water of considerable length it probably would not be difficult to assign the places in which the different neutral compounds yielded to, or resisted, decomposition. Sulphate of barytes, in all cases that I tried, required immediate contact with the wire: solution of sulphate of potash exhibited no marks of decomposition with the power of 150, when connected in a circuit of water ten inches in length, at four inches from the positive point; but when placed within two inches, its alkali was slowly repelled and its acid attracted.\*

Whenever bodies brought by artificial means into a high state of opposite electricities are made to restore the equilibrium, heat and light are the common consequences. It is

\* In this experiment, the water was contained in a circular glass basin two inches deep, the communication was made by pieces of amianthus of about the eighth of an inch in breadth. The saline solution filled a half ounce measure, and the distance between the solution and the water, at both points of communication, was a quarter of an inch. I mention these circumstances because the quantity of fluid and the extent of surface materially influence the result in trials of this kind. Water included in glass siphons forms a much less perfect conducting chain than when diffused upon the surface of fibrous nonconducting substances of much smaller volume than the diameter of the siphons. I attempted to employ siphons in some of my first experiments; but the very great inferiority of effect as compared with that of amianthus made me altogether relinquish the use of them.

perhaps an additional circumstance, in favour of the theory to state, that heat and light are likewise the result of all intense chemical action. And as in certain forms of the VOLTAIC battery, where large quantities of electricity of low intensity act, heat is produced without light; so in slow combinations there is an increase of temperature without luminous appearance.

The *effect of HEAT*, in producing combination, may be easily explained according to these ideas. It not only often gives more freedom of motion to the particles, but in a number of cases it seems to exalt the electrical energies of bodies; glass, the tourmalin, sulphur, all afford familiar instances of this last species of energy.

I heated together an insulated plate of copper and a plate of sulphur, and examined their electricities as their temperature became elevated: these electricities, scarcely sensible at  $56^{\circ}$  FAHRENHEIT to the condensing electrometer, became at  $100^{\circ}$  FAHRENHEIT capable of affecting the gold leaves without condensation; they increased in a still higher ratio as the sulphur approached towards its point of fusion. At a little above this point, as is well known from the experiments of the Dutch chemists, the two substances rapidly combine, and heat and light are evident.

Similar effects may be conceived to occur in the case of oxygene and hydrogene, which form water, a body apparently neutral in electrical energy to most other substances: and we may reasonably conclude that there is the same exaltation of power, in all cases of combustion. In general, when the different energies are strong and in perfect equilibrium, the combination ought to be quick, the heat and light intense, and

the new compound in a neutral state. This would seem to be the case in the instance just quoted ; and in the circumstances of the union of the strong alkalis and acids. But where one energy is feeble and the other strong, all the effects must be less vivid ; and the compound, instead of being neutral, ought to exhibit the excess of the stronger energy.

This last idea is confirmed by all the experiments which I have been able to make on the energies of the saline compounds with regard to the metals. Nitrate and sulphate of potash, muriate of lime, oxymuriate of potash, though repeatedly touched upon a large surface by plates of copper and zinc, gave no electrical charge to them ; subcarbonate of soda and borax, on the contrary, gave a slight negative charge, and alum and superphosphate of lime a feeble positive charge.

Should this principle on further enquiry be found to apply generally, the degree of the electrical energies of bodies, ascertained by means of sensible instruments, will afford new and useful indications of their composition.

#### IX. *On the Mode of Action on the Pile of VOLTA, with experimental Elucidations.*

The great tendency of the attraction of the different chemical agents, by the positive and negative surfaces in the VOLTAIC apparatus, seems to be to restore the electrical equilibrium. In a VOLTAIC battery, composed of copper, zinc, and solution of muriate of soda, all circulation of the electricity ceases, the equilibrium is restored if copper be brought in contact with the zinc on both sides : and oxygene and acids,

which are attracted by the positively electrified zinc, exert similar agencies to the copper, but probably in a slighter degree, and being capable of combination with the metal, they produce a momentary equilibrium only.

The electrical energies of the metals with regard to each other, or the substances dissolved in the water, in the VOLTAIC and other analogous instruments, seem to be the causes that disturb the equilibrium, and the chemical changes the causes that tend to restore the equilibrium ; and the phænomena most probably depend on their joint agency.

In the VOLTAIC pile of zinc, copper, and solution of muriate of soda, in what has been called its condition of electrical tension, the communicating plates of copper and zinc are in opposite electrical states. And with regard to electricities of such very low intensity, water is an insulating body : every copper-plate consequently produces by induction an increase of positive electricity upon the opposite zinc plate ; and every zinc plate an increase of negative electricity on the opposite copper-plate : and the intensity increases with the number, and the quantity with the extent of the series.

When a communication is made between the two extreme points, the opposite electricities tend to annihilate each other ; and if the fluid medium could be a substance incapable of decomposition, the equilibrium, there is every reason to believe, would be restored, and the motion of the electricity cease. But solution of muriate of soda being composed of two series of elements possessing opposite electrical energies, the oxygene and the acid are attracted by the zinc, and the hydrogene and the alkali by the copper. The balance of power is momentary only ; for solution of zinc is formed, and the hydro-

gene disengaged. The negative energy of the copper and the positive energy of the zinc are consequently again exerted, enfeebled only by the opposing energy of the soda in contact with the copper, and the process of electromotion continues, as long as the chemical changes are capable of being carried on.

This theory in some measure reconciles the hypothetical principles of the action of the pile adopted by its illustrious inventor, with the opinions concerning the chemical origin of **GALVANISM**, supported by the greater number of the British philosophers, and it is confirmed and strengthened by many facts and experiments.

Thus the VOLTAIC pile of 20 pairs of plates of copper and zinc exhibits no permanent electromotive power when the connecting fluid is water free from air;\* for this substance does not readily undergo chemical change, and the equilibrium seems to be capable of being permanently restored through it. Concentrated sulphuric acid, which is a much more perfect conductor, is equally inefficient, for it has little action upon zinc, and is itself decomposed only by a very strong power. Piles, containing as their fluid element either pure water or sulphuric acid, will undoubtedly give single shocks, and this effect is connected with the restoration of the equilibrium disturbed by the energies of the metals; but when their extreme plates are connected there is no exhibition, as in usual cases of electromotion. Water containing loosely combined oxygene is more efficient than water containing common air, as it enables

\* The experiments proving this fact, and the other analogous facts in this page, may be seen detailed in Nicholson's Journal, 4to. Vol. IV. page 338 and 394; and Phil. Mag. Vol. X. page 40.

oxide of zinc to be formed more rapidly, and in larger quantities. Neutrosaline solutions which are at first very active, loose their energy in proportion as their acid arranges itself on the side of the zinc, and their alkali on that of the copper ; and I have found the powers of a combination nearly destroyed from this cause very much revived, merely by agitating the fluids in the cells and mixing their parts together. Diluted acids, which are themselves easily decomposed, or which assist the decomposition of water, are above all other substances powerful ; for they dissolve the zinc, and furnish only a gaseous product to the negative surface, which is immediately disengaged.

There are other experiments connected with very striking results, which offer additional reasons for supposing the decomposition of the chemical menstrua essential to the continued electromotion in the pile.

As when an electrical discharge is produced by means of small metallic surfaces in the VOLTAIC battery, (the opposite states being exalted,) *sensible* heat is the consequence, it occurred to me, that if the decomposition of the chemical agents was essential to the balance of the opposed electricities, the effect, in a saline solution, of this decomposition, and of the transfer of the alkali to the negative side, and of the acid to the positive side, ought, under favourable circumstances, to be connected with an increase of temperature.

I placed the gold cones, which have been so often mentioned, in the circuit of the battery with the power of 100, I filled them with distilled water, and connected them by a piece of moistened asbestos, about an inch in length and  $\frac{1}{6}$  of an inch diameter ; I provided a small air-thermometer capable

of being immersed in the gold cones, expecting (if any) only a very slight change of temperature; I introduced a drop of solution of sulphate of potash into the positive cone: the decomposition instantly began: potash passed rapidly over into the negative cone, heat was immediately sensible; and in less than two minutes the water was in a state of ebullition.

I tried the same thing with a solution of nitrate of ammonia, and in this instance the heat rose to such an intensity as to evaporate all the water in three or four minutes, with a kind of explosive noise; and at last actual inflammation took place, with the decomposition and dissipation of the greatest part of the salt.\*

That the increase of the conducting power of the water by the drop of saline solution had little or nothing to do with the effect, is evident from this circumstance. I introduced a quantity of strong lixivium of potash into the cones, and likewise concentrated sulphuric acid, separately, which are better conductors than solutions of the neutral salts; but there was very little sensible effect.

The same principles will apply to all the varieties of the electrical apparatus, whether containing double or single plates; and if the ideas developed in the preceding sections be correct, one property operating under different modifications is the universal cause of their activity.

\* In this process ammonia was rapidly given off from the surface of the negative cone, and nitrous acid from that of the positive cone, and a white vapour was produced by their combination in the atmosphere above the apparatus.

*X. On some general Illustrations and Applications of the foregoing Facts and Principles, and Conclusion.*

The general ideas advanced in the preceding pages are evidently directly in contradiction to the opinion advanced by FABRONI, and which, in the early stage of the investigation, appeared extremely probable, namely, that chemical changes are the *primary* causes of the phænomena of GALVANISM.

Before the experiments of M. VOLTA on the electricity excited by the mere contact of metals were published, I had to a certain extent adopted this opinion; but the new facts immediately proved that another power must necessarily be concerned; for it was not possible to refer the electricity exhibited by the apposition of metallic surfaces to any chemical alterations, particularly as the effect is more distinct in a dry atmosphere, in which even the most oxidable metals do not change, than in a moist one, in which many metals undergo chemical alteration.

Other facts likewise soon occurred demonstrative of the same thing. In the VOLTAIC combination of diluted nitrous acid, zinc and copper, as is well known, the side of the zinc exposed to the acid is positive. But in combinations of zinc, water and diluted nitric acid, the surface exposed to the acid is negative; though if the *chemical* action of the acid on the zinc had been the cause of the effect, it ought to be the same in both cases.

In mere cases of chemical change likewise electricity is never exhibited. Iron burnt in oxygene gas, properly connected with a condensing electrometer, gives no charge to it during the process. Nitre and charcoal deflagrated in com-

munication with the same instrument do not by their agencies in the slightest degree affect the gold leaves. Solid pure potash and sulphuric acid made to combine in an insulated platina crucible produce no electrical appearances. A solid amalgam of bismuth and a solid amalgam of lead become fluid when mixed together: the experiment, I find, is connected with a diminution of temperature, but with no exhibition of electrical effects. A thin plate of zinc, after being placed upon a surface of mercury, and separated by an insulating body, is found positive, the mercury is negative: the effects are exalted by heating the metals; but let them be kept in contact sufficiently long to amalgamate, and the compound gives no signs of electricity. I could mention a great number of other instances of *pure chemical* action in which I have used all the means in my power to ascertain the fact, and the result has been constantly the same. In cases of effervescence, indeed, particularly when accompanied by much heat, the metallic vessels employed become negative, but this is a phænomenon connected with *evaporation*, the change of state of a body independent of chemical change, and is to be referred to a different law.\*

\* The change of the capacities of bodies in consequence of the alteration in their volumes, or states of existence by heat, is a continually operating source of electrical effects: and as I have hinted, page 36, it often interferes with the results of experiments on the electrical energies of bodies as exhibited by contact. It is likewise probably one of the sources of the capricious results of experiments of friction, in which the same body, according as its texture is altered, or its temperature changed, assumes different states with regard to another body. Friction may be considered as a succession of contacts, and the natural energies of bodies would probably be accurately exhibited by it, if the unequal excitation of heat or its unequal communication to the different surfaces did not interfere by altering unequally their electrical capacities. Of the elements of flint glass, silex is slightly negative with

I mentioned the glass plates of BECCARIA as affording a parallel to the case of combination in consequence of the different electrical states of bodies. In GUYTON DE MORVEAU's experiments on cohesion, the different metals are said to have adhered to mercury with a force proportional to their chemical affinities. But the other metals have different electrical energies, or different degrees of the same electrical energy with regard to this body; and in all cases of contact of mercury with another metal, upon a large surface, they ought to adhere in consequence of the difference of their electrical states, and that with a force proportional to the exaltation of those states. Iron, which M. GUYTON found slightly adhesive, I find exhibits little positive electricity after being laid upon a surface of mercury, and then separated. Tin, zinc, and copper, which adhere much more strongly, communicate higher charges to the condensing electrometer: I have had no instrument sufficiently exact to measure the differences: but it would seem that the adhesion from the difference of electrical states must have operated in these experiments,\* which being proportional to the electrical energies are, on the hypothesis before stated, proportional to the chemical affinities. How far cohesion in general may be influenced or occasioned by this effect of the difference of the electrical energies of bodies is a curious question for investigation.

Many applications of the general facts and principles to regard to the metals, the soda is positive; and in contacts of glass with metals I find it exhibits the excess of the energy of the alkali: the case, as is well known, is the same in friction, the amalgam of the common machine is essential to its powerful excitation.

\* Amalgamation undoubtedly must have interfered; but the *general* result seems to have been distinct.

the processes of chemistry, both in art and in nature, will readily suggest themselves to the philosophical enquirer.

They offer very easy methods of separating acid and alkaline matter, when they exist in combination, either together or separately, in minerals; and the electrical powers of decomposition may be easily employed in animal and vegetable analysis.

A piece of muscular fibre, of two inches long and half an inch in diameter, after being electrified by the power of 150 for five days, became perfectly dry and hard, and left on incineration no saline matter. Potash, soda, ammonia, lime, and oxide of iron were evolved from it on the negative side, and the three common mineral acids and the phosphoric acid, were given out on the positive side.

A laurel leaf treated in the same manner, appeared as if it had been exposed to a heat of  $500^{\circ}$  or  $600^{\circ}$  FAHRENHEIT, and was brown and parched. Green colouring matter, with resin, alkali, and lime, appeared in the negative vessel: and the positive vessel contained a clear fluid, which had the smell of peach blossoms; and which, when neutralized by potash, gave a blue-green precipitate to solution of sulphate of iron; so that it contained vegetable prussic acid.

A small plant of mint, in a state of healthy vegetation, was made the medium of connection in the battery, its extremities being in contact with pure water; the process was carried on for 10 minutes: potash and lime were found in the negatively electrified water, and acid matter in the positively electrified water, which occasioned a precipitate in solutions of muriate of barytes, nitrate of silver, and muriate of lime. This plant recovered after the process: but a similar one, that had been

electrified for four hours with like results, faded and died.\* The facts shew that the electrical powers of decomposition act even upon living vegetable matter; and there are some phænomena which seem to prove that they operate likewise upon living animal systems. When the fingers, after having been carefully washed with pure water, are brought in contact with this fluid in the positive part of the circuit, acid matter is rapidly developed, having the characters of a mixture of muriatic, phosphoric, and sulphuric acids: and if a similar trial be made in the negative part, fixed alkaline matter is as quickly exhibited.

The acid and alkaline tastes produced upon the tongue, in **GALVANIC** experiments, seem to depend upon the decomposition of the saline matter contained in the living animal substance, and perhaps in the saliva.

As acid and alkaline substances are capable of being separated from their combinations in living systems by electrical powers, there is every reason to believe that by converse methods they may be likewise introduced into the animal œconomy, or made to pass through the animal organs: and the same thing may be supposed of metallic oxides; and these ideas ought to lead to some new investigations in medicine and physiology.

It is not improbable that the electrical decomposition of the neutral salts in different cases may admit of œconomical uses.

\* Seeds, I find, when placed in pure water in the positive part of the circuit, germinate much more rapidly than under common circumstances; but in the negative part of the circuit they do not germinate at all. Without supposing any peculiar effects from the different electricities which however *may* operate, the phænomenon may be accounted for from the saturation of the water near the positive metallic surface with oxygene, and of that near the negative surface with hydrogene.

Well burned charcoal and plumbago, or charcoal and iron, might be made the exciting powers; and such an arrangement if erected upon an extensive scale, neutrosaline matter being employed in every series, would, there is every reason to believe, produce large quantities of acids and alkalies with very little trouble or expence.

Ammonia and acids capable of decomposition, undergo chemical change in the VOLTAIC circuit only when they are in very concentrated solution, and in other cases are merely carried to their particular points of rest. This fact may induce us to hope that the new mode of analysis may lead us to the discovery of the *true* elements of bodies, if the materials acted on be employed in a certain state of concentration, and the electricity be sufficiently exalted. For if chemical union be of the nature which I have ventured to suppose, however strong the natural electrical energies of the elements of bodies may be, yet there is every probability of a limit to their strength: whereas the powers of our artificial instruments seem capable of indefinite increase.

Alterations of electrical equilibrium are continually taking place in nature; and it is probable that this influence, in its faculties of decomposition and transference, considerably interferes with the chemical alterations occurring in different parts of our system.

The electrical appearances which precede earthquakes and volcanic eruptions, and which have been described by the greater number of observers of these awful events, admit of very easy explanation on the principles that have been stated.

Besides the cases of sudden and violent change, there must be constant and tranquil alterations in which electricity is

concerned, produced in various parts of the interior strata of our globe.

Where pyritous strata and strata of coal-blende occur, where the pure metals or the sulphurets are found in contact with each other, or any conducting substances, and where different strata contain different saline menstrua, electricity must be continually manifested; and it is very probable, that many mineral formations have been materially influenced, or even occasioned by its agencies.

In an experiment that I made of electrifying a mixed solution of muriates of iron, of copper, of tin, and of cobalt, in a positive vessel, distilled water being in a negative vessel, all the four oxides passed along the asbestos, and into the negative tube, and a yellow metallic crust formed on the wire, and the oxides arranged themselves in a mixed state round the base of it.

In another experiment, in which carbonate of copper was diffused through water in a state of minute division, and a negative wire placed in a small perforated cube of zeolite in the water, green crystals collected round the cube; the particles not being capable of penetrating it.

By a multiplication of such instances the electrical power of transference may be easily conceived to apply to the explanation of some of the principal and most mysterious facts in geology.

And by imagining a scale of feeble powers, it would be easy to account for the association of the insoluble metallic and earthy compounds, containing acids.

Natural electricity has hitherto been little investigated,

except in the case of its evident and powerful concentration in the atmosphere.

Its slow and silent operations in every part of the surface will probably be found more immediately and importantly connected with the order and oeconomy of nature; and investigations on this subject can hardly fail to enlighten our philosophical systems of the earth; and may possibly place new powers within our reach.

#### EXPLANATION OF THE FIGURES.

##### Plate I.

Fig. 1, Represents the agate cups, mentioned page 4.

Fig. 2, Represents the gold cones, page 6.

Fig. 3, Represents the glass tubes, and their attached apparatus, page 21.

Fig. 4, Represents the two glass tubes, with the intermediate vessel, page 22.

In all the figures A B denote the wires, rendered one positively, the other negatively electrical; and C the connecting pieces of moistened amianthus.

Fig. 1.

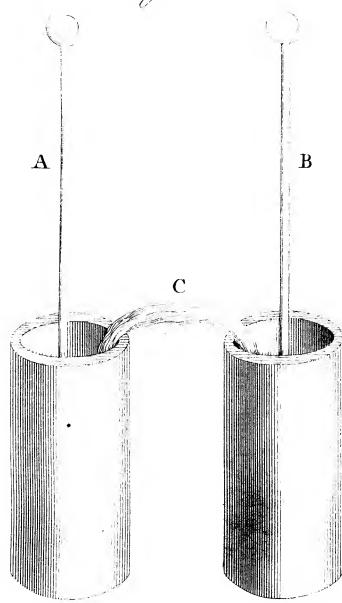


Fig. 2.

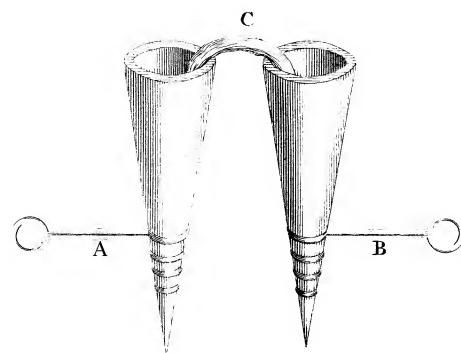


Fig. 3.

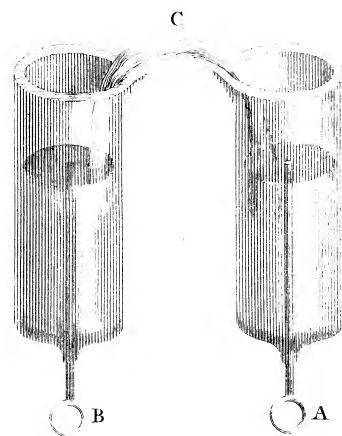


Fig. 4.

